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Nitrous oxide and ammonia emissions from N fertilization of maize crop under no-till in a Cerrado soil

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ABSTRACT

The low natural fertility of Oxisols in the Cerrado region makes some crops in this region very dependent on high rates of synthetic N-fertilizers, which are of growing environmental concern as a major source of N_2O emissions in agriculture. In a field experiment, we quantified direct N_2O emissions and NH_3 volatilization (a source of indirect N_2O emissions) from surface-applied N fertilizer on a no-till maize (*Zea mays* L.) crop in Cerrado biome. We used four fertilizers at the rate of 120 kg N ha^{-1} as topdress-N (V4–V6 growth stage), which were regular urea, urea + zeolite, calcium nitrate and ammonium sulfate, and a non-topdressed control. The total N losses as volatilized NH_3 ranged from 2.2% (calcium nitrate) to 4.5% (urea + zeolite). The N loss as volatilized NH_3 from urea was very low (3.2%), with no significant difference between urea + zeolite, ammonium sulfate and calcium nitrate. Significantly, higher cumulated N_2O emissions were observed with ammonium sulfate than with the control. No significant differences among fertilizers were found for emission factor (EF), which was 0.20% on average (0.14–0.26%), indicating that use of IPCC default EF (1.00%) would substantially overestimate N_2O emission. Free drainage and acidity of Oxisols and occurrence of dry spells, known as '*veranicos*', are characteristics of Cerrado biome that may naturally mitigate N_2O emissions.

1. Introduction

The Cerrado is the second largest biome in Brazil and the largest tropical savanna in America, representing 2 million km^2 (IBGE, 2014), of which almost half exists on Oxisols (EMBRAPA, 2006). This biome is the most important for Brazilian agriculture because of the 1.1 million km^2 of soils considered legally apt for expansion of agriculture, 72% are located in Cerrado region (Coelho, 2011). However, the low natural fertility of Oxisols in Cerrado makes most crops in this region very dependent on high rates of synthetic fertilizers, including those containing N (Lopes, 1996).

The increasing use of N-fertilizers is of growing environmental concern, since they are a major source of nitrous oxide (N_2O) emissions in agriculture (Klein et al., 2007). Nitrous oxide is a greenhouse gas (GHG) that has a half-life of 131 years (Hartmann et al., 2013) and also causes depletion in the ozone layer in atmosphere (Ravishankara et al., 2009). This has direct implications for global GHG emissions in Brazil, which, as a signatory of the Copenhagen Accord, has committed to cut by 36.1–38.9% of GHG emissions considering the projected levels in 2020 (Lau et al., 2012). Since agriculture is one of the most important economic sectors in Brazil, it is essential to adopt specific measures aimed at mitigating emissions associated with agricultural activity, such as choosing N-fertilizers that emit as little as possible N_2O. Moreover, there is a need of more precise estimates for tropical regions of the fraction of fertilizer-N emitted as N_2O, *i.e.*, emission factors (EF), which are a basic parameter for developing national inventories of GHG emissions.

The lack of available data to provide appropriate country-specific emission factors (direct and indirect N_2O emissions) is one of the main uncertainties in developing of GHG inventories (Klein et al., 2007). Obtaining these data is an indispensable step for Brazil towards the use of Tier 2 IPCC equations with country-specific EFs instead of Tier 1 equations with default EFs, thus improving the precision of N_2O emissions in its national inventory. According to IPCC guidelines, the default EF for N application of mineral fertilizers is 1.00% for direct N_2O emissions with an uncertainty range of 0.30–3.00%. However, some field studies have shown that

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these IPCC default values are overestimated for Brazil, including those for the Cerrado region (Davidson et al., 2001; Metay et al., 2007; Jantalia et al., 2008).

Nitrous oxide emission from N-fertilizers occurs directly (nitrification and denitrification) and indirectly. The indirect pathways of N_2O emission involve off-site emissions after N losses by NH_3 volatilization, leaching, runoff and harvest of crops (Nevison, 2000). It is estimated that indirect N_2O emissions account for approximately one-third of the agricultural N_2O source (Mosier et al., 1998). In the Cerrado biome, there are uncertainties on the direct and indirect N_2O emissions, which come from (i) the occurrence of dry spells from one to three weeks during the peak rainy season, locally called "*veranico*" (Kornelius et al., 1979); (ii) the typical occurrence of well drained and aerated soils in Cerrado (Bustamante et al., 2009); (iii) the increase of no-till area with placement of fertilizers on the soil surface in contact with undecomposed plant residues; and (iv) the possible use of different types of N fertilizer.

The N fertilizer most widely applied in Brazil is urea (ANDA, 2011), owing to its high N content, which reduces its transportation cost, as well as its relatively simple production by fertilizer industry (Cantarella and Marcelino, 2007). However, the use of this N source can result in high N losses by NH_3 volatilization associated with urease activity, representing an economic loss and considerable environmental concern (Fenn and Hossner, 1985; Soares et al., 2012). Use of N sources other than urea, such as some ammonium or nitrate salts, or modified forms of urea, may represent alternatives favoring increased N-use efficiency and/or mitigation of direct and indirect N_2O emissions. For instance, the use of NO_3^--based fertilizers, such as calcium nitrate, can reduce ammonia volatilization, but their greater susceptibility to denitrification may lead to increased emissions of N_2O (Harrison and Webb, 2001). Another possible technology for mitigating direct and indirect N_2O emission is the use of finely ground zeolites added to urea during fabrication of the granules. Zeolites are negatively charged alumino-silicates which can sorb NH_4^+, reducing N-NH_3 loss by volatilization (Kithome et al., 1999; Werneck et al., 2012). The use of zeolite as soil amendment is considered as a strategy to reduce N_2O emissions from soil (Zaman and Nguyen, 2010).

Our aim was to quantify, under field condition, the N losses by N_2O emissions (direct losses) and NH_3 volatilization (a source for indirect losses) after broadcasting of fertilizers in an Oxisol cultivated with maize (*Zea mays* L.) under a no-till system in Cerrado biome.

2. Material and methods

The field experiment was conducted in the 2012–2013 cropping season in Luis Eduardo Magalhães, a municipality located in the extreme west of the State of Bahia, Brazil, within the ecosystem of the Cerrado biome (12°00′S, 46°03′W and altitude of 844 m). More specifically, the predominant vegetation in the region, considering the canopy cover, is Cerrado *sensu stricto* (typical scrubland with small trees). Climatologically, the area belongs to the tropical megathermal zone, or Köppen's Aw (a tropical climate with a dry winter and an average temperature of the coldest month >18 °C). The mean annual rainfall from 2008 to 2013 in the area was 1473 mm, with an annual distribution that peaks in the period from October to March and a severe dry season in the period from April to September.

The soil in the experimental area is an Oxisol (Xanthic Hapludox) based on the U.S. Soil Taxonomy (Soil Survey Staff, 2010). This area has been used for twenty years for commercial production of maize and soybean [*Glycine max* (L.) Merr.] in rotation since substitution of the Cerrado vegetation by agriculture. No-till was adopted eleven years before the field experiment. Soybean was the crop in the year before the experiment with maize. Physical and chemical soil properties are shown in Table 1.

Three months before establishing the experiment, phosphorus was applied as single superphosphate at 35 kg P ha^{-1}. Maize was mechanically sown on December 4, 2012. Ammonium sulfate was applied as banded starter fertilizer (40 kg N ha^{-1}) placed below and to the side of the seed position. Potassium (125 kg K ha^{-1}) was broadcast 13 days after sowing as potassium chloride.

The experimental treatments consisted of four different N-fertilizers broadcast on the soil surface at the V4-V6 growth stage of the maize and one control without N fertilizer at this time. The N-fertilizers were (i) regular urea, (ii) urea granulated with powdered zeolite in mass proportion of 4:1 (urea + zeolite), (iii) calcium nitrate and (v) ammonium sulfate. The N fertilizers were broadcast 15 days after sowing (DAS) at a rate of 120 kg N ha^{-1}. A randomized complete-block design with 6 replicates was used. Each plot was 10.0 m long by 5.6 m wide, considering 1.0 m of the extremities as borders. A row spacing of 0.70 m and 5 plants m^{-1} was used.

After application of the N-fertilizers, the plots received semi-open chambers for NH_3 volatilization measurement. The detailed description and validation of these chambers using ^{15}N recovery technique was reported in studies conducted by Araújo et al. (2009) and Jantalia et al. (2012). Briefly, the chamber consists of transparent polyethylene terephthalate bottle (carbonated soft-drink bottle 2 L) with the bottom removed, which is subsequently fixed on the top of the bottle. Inside each chamber, there was a 250 mm long wire designated to support a foam strip (2.5 cm × 25 cm, 3 mm thick) presoaked in acid solution and a plastic pot (60 mL) that contained the acid solution to keep a foam strip moist during sampling periods.

The chambers were placed in two positions considering the rows of maize plants. One chamber was located in the row of plants, *i.e.*, right beside two plants in the same row, and the second chamber was positioned in the center of the space between two rows of plants, *i.e.*, 35 cm from the stems. To ensure a better homogeneity of broadcasting of the fertilizers in the location of chambers, an area of 2.0 m long × 1.4 m wide was reserved inside each plot to receive a corresponding amount of fertilizer, which was very carefully spread to guarantee the uniformity of granules in soil surface. The foam strips were replaced 1, 2, 3, 5, 7, 10, 13, 17, 21, 25, 30 and 37 days after N-fertilization. The collected foam strips were transported inside the plastic pots to the laboratory and were then carefully transferred to Erlenmeyers flasks by rinsing the plastic pots with 40 mL of deionized water. The Erlermeyer flasks were shaken for 20 min at 220 rpm on an orbital shaker. After that, the content was transferred to 100 mL volumetric flasks with careful washing of the foams and the flasks completed to 100 mL. An 10 mL aliquot of this solution was used for analysis of NH_4^+ by steam distillation (Keeney and Nelson, 1982). The amount of N recovered in this analysis was multiplied by a factor of 1.47 calculated considering the efficiency of chambers, calibrated with the ^{15}N technique (Jantalia et al., 2012).

Table 1
Physical and chemical properties of a Xanthic Hapludox under no-till system from Bahia State, Brazil.

Property	0–10 cm	10–20 cm
Sand (g kg^{-1})	737	754
Silt (g kg^{-1})	49	28
Clay (g kg^{-1})	214	218
Bulk density (g cm^{-3})	1.41	1.48
pH (H_2O)	5.2	5.1
Organic C (g kg^{-1})	6.4	4.2
Total N (g kg^{-1})	0.2	0.2

For tracking soil N_2O fluxes, the gas sampling was performed between 09:00 hours and 10:00 hours, following the recommendation of Alves et al. (2012) to best represent the daily mean flux. Before the application of the N fertilizer treatments, gas sampling for N_2O was made on five occasions (7, 6, 5, 4 and 1 day before topdress-N application) in the control plots. After fertilizer application N_2O fluxes were evaluated daily from day 1 to day 13. Subsequently, the frequency decreased to four or three times a week (week 3 to week 5), two times a week (week 6), one time a week (week 7 to week 16) and 5 times during the last period of sampling (week 17 to week 38).

The N_2O fluxes were measured from the beginning of the experiment by using static chambers with sampling performed manually. One chamber was used in each plot, inserted in the space between two rows of maize. The chamber was composed of a rectangular metal frame (40 × 60 cm) with height of 7.5 cm, totally inserted in soil. In the top of this frame there was a trough (2.0 cm of width × 2.0 cm of height). During gas sampling, this trough was filled with water to ensure the sealing of the chamber after coupling to superior part, which consisted of a rectangular polyethylene tray of 40 × 60 cm and a height of 12 cm. These trays were fitted with a three-way Luer Lock tap for withdrawing of the gas samples. The sampling time was set to 30 min, one sample being taken immediately after coupling of superior and inferior parts of chamber and another one at the end of incubation time. A volume of ~40 mL of the air accumulated in the head space of each chamber was sampled with 60 mL syringes. Thereafter, syringes were coupled to a vacuum pump to transfer ~30 mL of the gas samples to 20 mL chromatographic vials. A volume of ~10 mL was initially discarded for purging of the pumping system. Analyses of N_2O concentrations were performed using a gas chromatograph equipped with an electron capture detector and a back-flush system (Jantalia et al., 2012).

During the experimental period, daily rainfall was recorded by a pluviometer installed in the center of the experimental area. At the time of gas sampling, the temperatures of the air outside and inside the chambers were recorded. Soil samples were taken (0–10 cm depth) for evaluation of soil moisture and mineral N content, twice before N fertilization and every week for the first month after N fertilizer addition and subsequently less frequently (Fig. 1). The soil samples were frozen immediately after sampling and posteriorly transported to laboratory for NO_3^- and NH_4^+ and water content analyses. 20 g of the fresh soil were used to determine the content of soil mineral N, which was extracted with 60 mL of 2 mol L^{-1} K_2SO_4 after 1 h on a rotary shaker at 220 rpm. The supernatant was filtered and the NO_3^- and NH_4^+ concentrations were determined in the resultant solution by UV spectrometry. For NO_3^- determination, the procedures described by Miyazawa et al. (1985) were used, but using the wavelengths 220 and 275 nm. The absorbance at 275 nm was multiplied by two and then subtracted from the absorbance at 220 nm to determine the absorbance of NO_3^-, as described by Olsen (2008). For determination of NH_4^+, the salicylate-hypochlorite procedure was followed (Kempers and Zweers, 1986). A 10 g aliquot of humid soil was oven-dried (105 °C) to determine the water content. Soil samples for the calculation of bulk density were also taken from the area. Soil porosity was estimated assuming a soil particle density of 2.68 kg dm^{-3} (Kiehl, 1979). The value of water-filled pore space (WFPS) was then calculated by using values of soil water content and bulk and particle densities, as described in Jantalia et al. (2008).

A ^{15}N-aided N balance study was performed for ammonium sulfate, urea and urea + zeolite to determine the recovery of fertilizer-N by maize. For these treatments, a microplot was established in an area of 2.8 m^2 (1.4 m width × 2 m of length) in a central position of each fertilized plot (each repetition). For this study, ^{15}N-labeled fertilizers were used with enrichments of 1.0 atom% ^{15}N in excess for urea and urea + zeolite and 0.67 atom% excess for ammonium sulfate. Labeled calcium nitrate was not available to be included in this ^{15}N study. At the harvest of maize, 150 days after sowing, 5 plants corresponding to 1.0 m of the central row of the ^{15}N-labelled microplot were collected. The grain of these plants was separated and weighed. The remaining material (straw + cob) was also weighed and finely chopped. Subsamples of grain and straw + cob were dried in a forced-air oven at 65 °C for 48 h, reweighed and ground (Wiley mill, 2 mm sieve). The dry plant material was then powder-milled and analyzed for total N and ^{15}N (Arnold and Schepers, 2004), following the procedures described by Ramos et al. (2001). Calculation of the N-fertilizer recovered in the plants was performed as described by Lessa et al. (2014).

The data for N_2O emissions and NH_3 volatilization were submitted to analysis of variance (ANOVA), and the means compared using Tukey's HSD test ($\alpha = 0.05$). ANOVA was carried out after determining the normality of errors (Shapiro–Wilk's test) and variance homogeneity (Bartlett's test) of data. The statistical analyses were performed using the R software (R Development Core Team, 2010).

3. Results and discussion

After N fertilization, no differences between N_2O fluxes from topdressed treatments and the non-topdressed control were observed during the period between day 0 and day 10 after topdress-N application, except for calcium nitrate in the first 2 days (Fig. 1A). This lack of fertilizer induced-fluxes of N_2O can be attributed to the dry spell after fertilizer application, which caused a decrease in WFPS from 39% before topdressing to 17% at the end of this initial period (Fig. 1C). From day 10 to day 20 after N application, small N_2O fluxes from urea, urea + zeolite and ammonium sulfate were observed following the rainfall events (<30 mm). It is possible to infer that N_2O emission in this period was due predominantly to the nitrification process, *i.e.*, the aerobic oxidation of ammonium to nitrite and then to nitrate which produces N_2O as byproduct (Ussiri and Lal, 2013). During this initial period, the concomitant occurrence of denitrification was probably restricted owing to the absence of anaerobic microsites within soil microaggregates (Sey et al., 2008). The predominant contribution of nitrification to N_2O production is supported in general by the occurrence of N_2O fluxes (Fig. 1A) with a concomitant decrease in soil NH_4^+ concentration in treatments other than that of ammonium sulfate (Fig. 1D) and the increase of soil NO_3^- content (Fig. 1E). The N_2O emission in this period through nitrification was favored by adequate soil aeration, indicated by values of WFPS <38% (Fig. 1C). Additionally, the lower fluxes in this period for calcium nitrate (Fig. 1A), which does not undergo nitrification, confirms that the N_2O production was from nitrification of NH_4^+ and NH_4^+-forming N-fertilizers (ammonium sulfate, urea and urea + zeolite).

The occurrence of a peak of N_2O flux occurred only 36 days after topdress-N application, caused by heavy rainfall of 110 mm in 24 h (Fig. 1A and C). This indicated that this peak was a rare occasion of N_2O production through denitrification, *i.e.*, an anaerobic microbial reduction of NO_3^- (*e.g.*, Robertson and Tiedje, 1987). Evidence of the occurrence of denitrification was the existence of a N_2O peak even for calcium nitrate, which does not undergo nitrification. The late occurrence of this peak showed that even at low content of NO_3^- in soil (Fig. 1E) significant N_2O fluxes can occur caused owing to suboptimal soil oxygenation induced by intense rainfall (Fig. 1C). The relatively low values of WFPS after the precipitation event indicate free soil drainage (Fig. 1C), which suggests that denitrification occurred more intensely inside microaggregates with

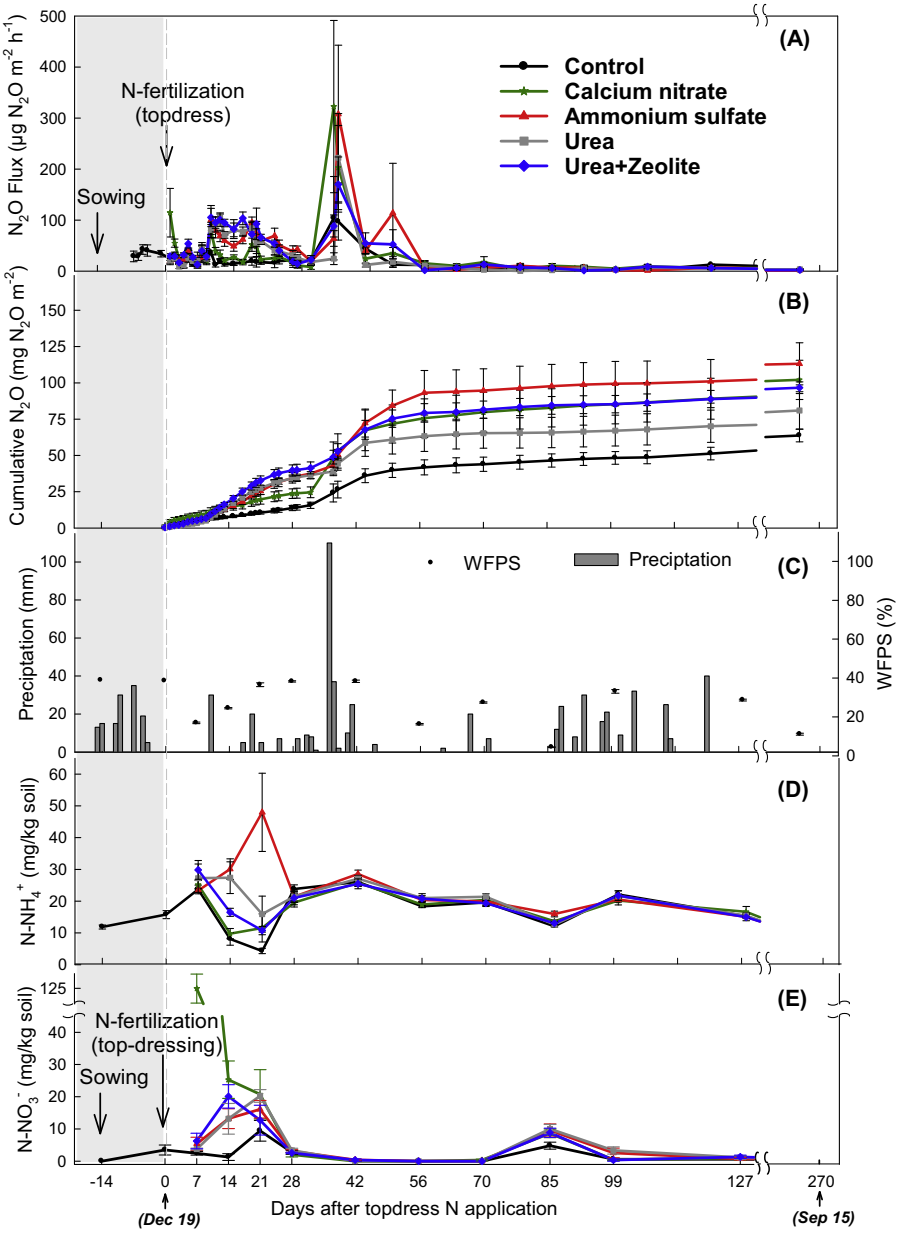

Fig. 1. Fluxes (A) and cumulated emissions (B) of N_2O from N-fertilizers applied to no-till maize in an Oxisol in Cerrado region. Rainfall and water-filled pore space (WFPS) data (C) are presented along with soil NH_4^+ (D) and NO_3^- (E) contents. Bars are standard error of mean. The gray area in the figure indicates the period pre-fertilization (topdress-N), *i.e.*, period before treatment application.

microsites saturated with water after intense rainfall (Sey et al., 2008).

Our results showed that there was a significantly higher cumulative N_2O emission with ammonium sulfate compared to the non-topdressed control (Fig. 1B, Table 2). The positive charges of NH_4^+ from ammonium sulfate may increase its probability of being adsorbed for longer time in soil, increasing consequently the possibility of conversion to N_2O. In a different hypothetical scenario, with more rain and low soil drainage, a higher cumulated N_2O emission from calcium nitrate would be expected due to

Table 2
N_2O emission from N-fertilizers applied to no-till maize in an Oxisol in the Cerrado region and the respective estimates of the fraction of the fertilizer N lost as N_2O.

Treatment	Cumulated emission (mg N_2O m^{-2})	Cumulated emission/yield (g N_2O Mg^{-1} grains)	Emission factor (kg N-N_2O kg^{-1} N-fertilizer)
Ammonium sulfate	113 ± 14a	171 ± 19a	0.0027 ± 0.0008a
Calcium nitrate	102 ± 14ab	162 ± 24a	0.0020 ± 0.0006a
Urea + zeolite	97 ± 4ab	149 ± 5a	0.0020 ± 0.0002a
Urea	81 ± 13ab	127 ± 23a	0.0013 ± 0.0005a
Control	64 ± 4b	108 ± 8a	–
Mean	91	144	0.0020
	Confidence interval (α = 0.05)		(0.0014–0.0026)

Means (±standard errors) followed by different letters are significantly different based on Tukey's HSD test (α = 0.05).

anaerobically-induced denitrification of readily available NO_3^- in comparison to NH_4^+ and NH_4^+-forming N-fertilizers.

Maize grain yield in our study ranged from 5.9 Mg ha^{-1} (control) to 6.5 Mg ha^{-1} (ammonium sulfate), but without significant differences among fertilizers (data not shown). Considering these results, we estimated that mean cumulated emission by yield ranged from 108 g N_2O per Mg of grain (control) to 171 g N_2O per Mg of grain (ammonium sulfate), without significant differences among treatments (Table 2). This kind of information can be useful for life-cycle analysis or ecobalance of grain production in terms of GHG emissions.

No significant differences among EFs for fertilizers applied in this present study were found (Table 2). The estimated mean EF was 0.20%, with a confidence interval of 0.14–0.26%. This result suggested that use of IPCC default EF (1.00%) would substantially overestimate direct N_2O emissions. The EFs estimated in our study are even below the threshold of uncertainty indicated by IPCC, which is 0.30% (Klein et al., 2007). Our results are in agreement with previous reports showing that higher N_2O emissions under no-till only occur in poorly-aerated soils (Rochette, 2008). For instance, in no-till soils with adequate aeration from Cerrado region, Metay et al. (2007) found EFs of 0.03%, which is substantially lower than the mean value found in present study (0.20%) and is only one-tenth of the minimum value of uncertainty range of IPCC (0.30%). Other studies also indicated that emissions for Brazilian tropical soils commonly having free drainage are significantly lower compared to soils with poor drainage (Davidson et al., 2001) and that use of IPCC default EFs overestimates significantly the real emissions (de Morais et al., 2013; Jantalia et al., 2008). The main reason for these lower EFs obtained in literature and our study is most likely to be the free drainage of most Brazilian tropical soils, which mitigates N_2O emission (Bustamante et al., 2009). Additionally, high evapotranspiration in the Cerrado region (Cochrane, 1978) is another possible factor contributing to rapid soil drying and consequently to mitigation of N_2O emission. Therefore, the rare occurrence of denitrification peaks with more frequent N_2O emission derived from nitrification is usual for Cerrado soils (Bustamante et al., 2009; Varella et al., 2004). The rapid drainage of water in Cerrado soils, even in the wet season, is due to their stable microaggregation (Bustamante et al., 2009). This structure is a characteristic of Oxisols and is explained by the cementing action of Fe oxides (Volland-Tuduri et al., 2005).

The results of the present study, and those obtained by other authors for Brazil, indicated that soil drainage capacity is a determinant factor for N_2O emissions. This suggests that soil drainage classes should be taken into account for definition of specific EFs and its uncertainty range. Soil drainage mapping using models or remote sensed data, such as described by Bell et al. (1994) or Cialella et al. (1997) could be useful tools to estimate N_2O production in calculations for national inventories.

Additionally, another factor that may contribute to the low values of the N_2O emissions recorded in our study was the relative low initial soil pH 5.2 (Table 1). Compared to soil pH around neutrality, lower soil pH reduces nitrification (de Boer and Kowalchuk, 2001; Yao et al., 2011) and denitrification (Parkin et al., 1985). For instance, the low nitrification in our study is indicated by the low soil NO_3^- content (Fig. 1E) compared to soil NH_4^+ contents (Fig. 1D). This suggests that natural acidity of Cerrado soils in Brazil can be a natural mitigating factor of N_2O in this biome if the soil does not receive lime frequently and has low buffer capacity.

The total volatilized NH_3 37 days after topdress-N application ranged from 5.7 kg N ha^{-1} (calcium nitrate) to 8.4 kg N ha^{-1} (urea + zeolite), which represents, respectively, only 2.2% and 4.5% of applied N, considering the volatilized NH_3 from control was 3.1 kg N ha^{-1} (Figs. 2 and 3). Total N loss as volatilized NH_3 from urea + zeolite was higher than that from calcium nitrate, ammonium sulfate or the control (Fig. 3). However, the N loss from regular urea was 6.9 kg N ha^{-1} (3.2% of applied N, subtracting the lost N as NH_3 from control), which was not significantly different from urea + zeolite, ammonium sulfate or calcium nitrate (Fig. 3). The percentage of N lost as volatilized NH_3 from urea in the present study is substantially lower than other results from literature. For instance, Bouwman et al. (2002) estimated that global emission from urea ranged from 18 to 26%. In Brazil, a study conducted in several sites in São Paulo State showed that percentage of N lost as volatilized NH_3 from urea ranged from 18 to 64% (Cantarella and Marcelino, 2007).

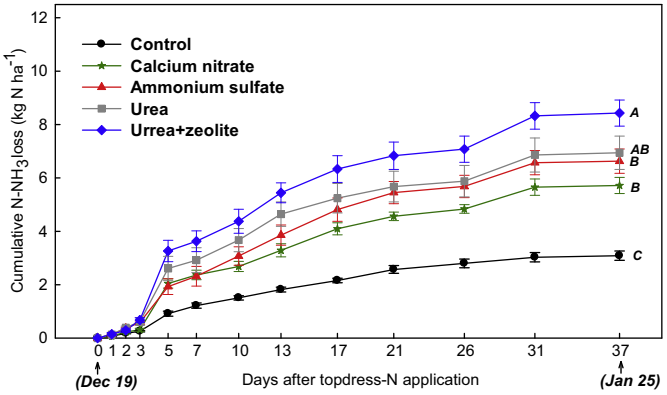

Fig. 2. Cumulative N loss as volatilized NH_3 from N-fertilizers applied to no-till maize in an Oxisol in Cerrado region. Bars are standard error of the means. Letters in day 37 indicate comparison of means based on Tukey's HSD test ($\alpha = 0.05$). Means followed by the same letter are not significantly different.

As was observed for initial period of N_2O flux, the relative low NH_3 volatilization from urea in the present study is likely due to the dry spell mainly in the first week after N application (Fig. 1C). The lack of rainfall after fertilization likely caused very low water content in the first millimeters of surface of the sandy soil (74% of sand) of our experiment (Table 1). This condition hampers NH_3 volatilization by not allowing immediate hydrolysis of fertilizers (Lara-Cabezas et al., 1992; Rochette et al., 2009; Volk, 1966). This is especially critical for the first week after fertilizers application, during which the most of NH_3 loss commonly occurs (*e.g.*, Akhtar and Naeem, 2012). This is evidenced mainly for the four days after N application (Fig. 2).

Another possible explanation for the relatively low volatilization of NH_3 from urea, as well from ammonium sulfate, would be

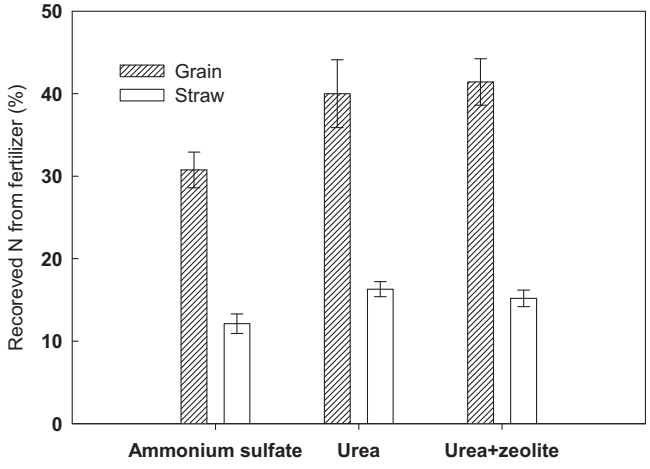

Fig. 3. Recuperation of topdress-^{15}N in straw and grains of maize.

the low soil pH (Table 1). This factor can reduce up to 72% the velocity of urea hydrolysis by urease, as observed in the classical experiment of van Slyke and Zacharias (1914). However, it is known that even in acidic soil, significant NH_3 losses may occur because of the increasing of pH in the vicinity of the applied urea because of the consumption of H^+ following enzymatic hydrolysis of urea to NH_4^+ (Overrein and Moe, 1967). Therefore, this reinforces that dry condition of soil surface was the main cause of low NH_3 volatilization from urea in the present study. In the case of ammonium sulfate, high NH_3 volatilization could only be expected when applied to soils of pH > 7.0 (Fenn and Hossner, 1985; Harrison and Webb, 2001).

Taking into consideration that level of NH_3 volatilization from urea was very low in our study, we hypothesize that zeolite could not express its effect in reducing N loss from urea in our study. In a scenario more propitious for NH_3 volatilization, it would be expected that zeolite would play a role in reducing N-NH_3 loss, as observed in previous studies (Kithome et al., 1999; Werneck et al., 2012). In a study conducted with a Brazilian Alfisol, under greenhouse conditions, the addition of zeolite to urea decreased NH_3 volatilization by 20% compared to regular urea and increased the N uptake by sorghum [*Sorghum bicolor* (L.) Moench] plants (Werneck et al., 2012). A study with poultry manure in Canada showed that the addition of zeolite placed on the surface of the manure reduced NH_3 losses by 44% during manure composting (Kithome et al., 1999). The main difference between these studies and ours is the level of NH_3 volatilization from treatments (urea or manure) non-amended with zeolite. Without zeolite, the N loss through NH_3 volatilization ranged from 47 to 62% in study of Kithome et al. (1999) and was 40% in the study of Werneck et al. (2012). These reports suggest that zeolites only have action under conditions where NH_3 volatilization is high. If owing to dry conditions $(NH_4)_2CO_3$ is not produced immediately following urea application, as indicated in our study (Figs. 1C and 2), NH_4^+ cannot be produced and then adsorbed onto negatively charged zeolite surfaces.

In the case of calcium nitrate, the NH_3 volatilization loss was low (2.2%) but still significantly greater than from the control (Figs. 2 and 3). A small NH_3 emission (1.8%) from calcium nitrate, applied at same rate (120 kg N ha^{-1}) was also observed by van der Weerden and Jarvis (1997) in a sandy loam soil from UK. Possible explanations for the small N loss from calcium nitrate are the fertilizer-induced residue mineralization (priming effect) leading to NH_3 emission and the remineralization of N, *i.e.*, a microbial immobilization of NO_3^- (Burger and Jackson, 2003) followed by ammonification resulting in small but significant production of NH_3. This is also indicated by the gradual increase of cumulative NH_3 through the time, especially between day 5 and day 37 days after N application (Fig. 2). One important factor to be considered for the N recycling is the presence of some plant residues on the soil surface derived from soybean, cultivated in the year before the maize. Part of the small volatilization from control plots (3.1 kg N ha^{-1}), as well from fertilized plots, was probably derived from these plant residues.

Other two possible forms of indirect N loss causing off-site N_2O emissions indicated by IPCC are the runoff and leaching (Klein et al., 2007). However, these sources are not expected to have contributed significantly to total emission in our experiment, taking into account the fate of N as analyzed by ^{15}N technique for ammonium sulfate, urea and urea + zeolite and also considering the landscape of the experimental site. The results of ^{15}N analyses showed that from total applied N, 12 to 16% were recovered in maize straw, 31 to 41% in grains (Fig. 3). The total recovery of N by maize from N-fertilizers, ranging from 43 to 57% in present study, is according to the reports in literature on N use efficiency by maize, showing values around 50% of applied N (Lara-Cabezas et al., 2004). Additionally, it is unlikely that substantial N losses through leaching occurred in present study. Under conditions very similar to ours in terms of precipitation (1315 mm), sand content (73%) and fertilizer rate (120 kg N ha^{-1}), a study on N leaching losses in an Oxisol cultivated with sugarcane (*Saccharum officinarum* L.) showed that N loss from fertilizer was only 54 g ha^{-1} (Ghiberto et al., 2011).

Our results suggest that indication of specific EFs for Cerrado condition is essential to project the environmental impact of GHG emission associated to agricultural expansion in the Cerrado region, which covers eight Brazilian states. Our experimental conditions are very representative of commercial production of maize in central region of Brazil, including landscape (very flat), typical vegetation of Cerrado (Cerrado *sensu stricto*) and soil acidity. For these specific conditions, more studies are needed to better understand the effect of other management practices associated with N fertilization in N_2O production, such as the impact of quantity and frequency of liming or irrigation, which may provide enough soil humidity for fertilizer hydrolysis and nitrification/denitrification intensification.

4. Conclusions

The present study was conducted under typical conditions of soil and climate for maize cropping in Cerrado region. Total losses of topdressed-N as volatilized NH_3 were relatively low (<4.5%). The N loss from urea was not significantly different from urea + zeolite, ammonium sulfate and calcium nitrate. Significant higher cumulative N_2O emission was observed with ammonium sulfate than from the non-fertilized control. No significant differences among fertilizers were found for the EF (mean of 0.20%), which was even below the threshold of uncertainty range indicated by IPCC (0.30–3.00%). These results indicate that use of IPCC default EF (1.00%) would substantially overestimate N_2O emission. The free draining and acidity of Oxisols and the occurrence of dry spells during the growing season are characteristics of the Cerrado biome that may naturally mitigate N_2O emissions. This may counterbalance the N_2O production from the use of high rates of N-fertilizers required for grain production in Cerrado soils.

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